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Thermal Study on Stabilizing the Combustion Front via Bimetallic Mn@Cu Tallates during Heavy Oil Oxidation

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ABSTRACT: Metal tallates are generating considerable interest as catalysts for thermally enhanced oil recovery. Meanwhile, *in situ* combustion is considered a promising thermally enhanced oil recovery method. It is still viewed as a complicated process as a result of its multiphasic, multicomponent, and multistep reactions occurring within it. In this study, we investigated the impact of Mn@Cu tallate on the heavy oil oxidation process to highlight its effect on stabilizing the combustion front using differential scanning calorimetry combined with an isoconversional principle for calculating the kinetic parameters of the process. The obtained data have showed that Mn@Cu tallate can play an important role in stabilizing the combustion front of *in situ* combustion, where it decreased the energy of activation of low- and high-temperature oxidation regions. As a result, the effective reaction rate constants in both regions increased as well.

INTRODUCTION

Many researchers nowadays focus on the exploitation of unconventional oil resources as a result of the shortage of conventional oils on one hand and market demand increasing on the other hand.^{1,2} It is well-known that heavy and extraheavy oils present a potential reserve of hydrocarbons among unconventional resources of energy in the world.³ However, their exploitation still faces a number of challenges because of their complex nature related to their high viscosity and density and their amount of undesirable elements.^{4,5} Recent developments in the exploitation of heavy and extra-heavy oils have led to the application of thermally enhanced oil recovery (ThEOR) methods as an alternative technology for increasing the recovery factor in hard reservoirs containing heavy and extra-heavy oils.⁶ The term ThEOR is generally understood to mean the application of heat to reservoirs containing unconventional oils to increase the temperature and pressure in situ and, therefore, improve the characteristics of the existing oil in place.' These methods are diverse and classified differently as steam-assisted gravity drainage (SAGD),⁸ cyclic steam stimulation (CSS),^{9,10} and *in situ* combustion.^{11,12} However, a growing body of literature has evaluated ThEOR techniques and highlighted the potential of in situ combustion among them.¹³

In broad terms, the *in situ* combustion process is the initiation of combustion within the reservoir of heavy oil, which results in a combustion front flowing heat in it and, therefore, decreasing the viscosity of the rest of oil in place.¹⁴ The main disadvantage of *in situ* combustion is the early breakdown of this combustion front, which is considered a crucial element in its successful application.¹⁵

For a better understanding of *in situ* combustion, many scientists have studied the chemical aspect of the process to show the reason behind combustion front breakdown.¹⁶ Generally, the process of *in situ* combustion includes two main regions called low-temperature oxidation (LTO) and high-temperature oxidation (HTO).¹⁷ During LTO, different hydrocarbons result from oxygen combination to oil components ending in what is known in the literature as fuel

deposition.¹⁸ This fuel burns at the HTO region¹⁹ and gives birth to a combustion front. Consequently, many hypotheses suggested the use of a catalyst to enhance the stabilization of this front for improving oil recovery at the end of the process.^{20,21}

Transition metals are widely used in oxidation processes and the petroleum industry as well.^{22,23} It has been demonstrated in different works that catalysts based on transition metals could be effective agents to promote the combustion front during the oxidation of heavy oil.^{24,25} Ramirez et al. have applied ionic liquids in in situ combustion and studied their influence on kinetic parameters of the process using a combustion tube.²⁶ The results demonstrated a significant decrease in viscosity, increment of oil production, and faster combustion front, adding to a reduction in sulfur, resin, and asphaltene contents in the produced oil. Another work has employed metal oxide nanoparticles, studied their effect by thermal analysis, and led to similar results in terms of reducing energy of activation of the process in the presence of nanoparticles compared to their absence.²⁷ In our previous works, we have applied oil-soluble catalysts in the process of heavy oil oxidation by means of differential scanning calorimetry (DSC) and showed good results in terms of decreasing the activation energy and increasing the frequency factor.^{28,29} Nevertheless, oil-soluble catalysts are considered as effective agents for the oxidation of heavy oils because of their high solubility in oil media. When it comes to catalyst choice, high selectivity and consistency with a positive impact on the surroundings in addition to the economic efficiency of the process are critical parameters to take into consideration. In this work, we have demonstrated the potential effect generated from the combination of copper and manganese tallates on the

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stabilization of the combustion front during the process of *in situ* combustion by applying DSC and an isoconversional principle for the calculation of kinetic parameters.

2. EXPERIMENTAL SECTION

2.1. Materials. The oil used in this research is biodegraded as shown on its gas chromatography-mass spectroscopy (GC-MS) analysis of its saturated fraction in Figure 1. It is clear that the amount



Figure 1. GC–MS analysis of the saturated fraction of Ashalcha heavy oil.

of the saturated fraction is low, as shown by indicated numbers on peaks. The heavy oil used in this study was extracted from the Ashalcha oilfield (Volga-Ural basin, Republic of Tatarstan, Russia) and characterized by means of the saturate, aromatic, resin, and asphaltene (SARA) analysis, as illustrated in Table 1. Organic solvents purer than 99.5% were purchased from Component Reactiv and used without additional purification. Inorganic salts and a pure quartz sand fraction of $43-64 \ \mu$ m were purchased from Sigma-Aldrich.

2.2. Sample Preparation. Copper and manganese carboxylates have been synthesized by exchange reactions between inorganic copper and manganese salts, sodium hydroxide, and distilled tall oil (DTO) as follows:

 $C_{17}H_{33}COOH + NaOH \rightarrow C_{17}H_{33}COONa + H_2O$

at 75-80 °C for 1.5 h, followed by

$$2C_{17}H_{33}COONa + Me(SO_4) \rightarrow (C_{17}H_{33}COO)_2Me + Na_2SO_4$$

at 75-80 °C for 1 h as well.

To determine the effect of Mn@Cu tallate, we prepared a mixture of heavy oil (10.0 wt %) with a pure quartz sand fraction of 43–64 μ m (90.0 wt %) referred in the text to S(0). In the case of catalytic experiments, the initial oil sample contained 2 wt % Mn–Cu tallates in different Mn tallate/Cu tallate ratios as follows: S₁(1:0), S₂(1:3), S₃(1:1), S₄(3:1), and S₅(0:1).

The molecular weight of asphaltenes in the studied oil was measured using the method of matrix-activated laser desorption/ ionization (MALDI) mass spectrometry. The studies were performed on an UltraFlex III TOF/TOF mass spectrometer (Bruker, Germany) with a time-of-flight analyzer, on a 2,5-dihydroxybenzoic acid matrix.

2.3. Thermal Analysis. The instrument employed to study the effect of a catalyst on the combustion process was a STA 449 F1 Jupiter (Netzsch) thermoanalyzer at a temperature range of 30-600 °C. The experiments were conducted at linear heating rates of 5, 10, 15, and 20 °C min⁻¹, under 50 mL min⁻¹ airflow. The data were

collected using the Proteus Analysis (version 5.2.1), NETZSCH Peak Separation (version 2010.09), and NETZSCH Thermokinetics 3.1 (version 06.08.2014) program package.

It is common knowledge that the kinetic study of oil combustion is complicated and hard because it contains multistep and parallel reactions in multicomponent and multiphasic media. For this reason, DSC presents a reliable tool for estimating kinetic parameters. The reaction rates during heavy oil oxidation are dependent upon the conversion degree and oxygen partial pressure, as shown in eq 1

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)P_{\mathrm{O}_2}{}^a(1-\alpha)^b \tag{1}$$

where α is the conversion degree (calculated by DSC fractional peaks), *b* is the reaction order, and *P*_{O2} is the oxygen partial pressure.

The rate constant k(T) is described by the Arrhenius law (eq 2).

$$k(T) = A e^{-E/RT}$$
(2)

In their work,^{17,30} Fassihi and Boussaid demonstrated that the reaction order in oil oxidation is equal to 1 (b = 1) relative to the oil concentration and oxygen partial pressure. In addition to this, the oxygen pressure is considered constant during the experiment because of the small size of the studied objects and the large volume of the DSC furnace thermoanalyzer at high airflow, which leads to eq 3 as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_{\mathrm{eff}}(1-\alpha) \tag{3}$$

where

 $k_{\rm eff} = k P_{\rm O_2}$

2.4. Kinetic Analysis. Through the use of the Kissinger method,³¹ we were able to obtain the energy of activation and pre-exponential factor of the process in both LTO and HTO regions. We chose this particular method because it is one of the most practical, feasible, and rapid ways to allow for the calculation of kinetic parameters using peak temperatures only at different heating rates without considering any baseline or peak profile choice. The final formula of this method is described by eq 4 as

$$\ln\left(\frac{\beta}{T_{\rm p}^{2}}\right) = -\frac{E}{R}\frac{1}{T_{\rm p}} + \ln(Af'(\alpha)) \tag{4}$$

where β is the heating rate and $T_{\rm p}$ is the peak temperature, respectively.

3. RESULTS AND DISCUSSION

3.1. Sample Selection. The aim of our study is to evaluate the effect of Cu@Mn tallates on the oxidation of heavy oil. Thus, we opted for DSC as a reliable method for calculating kinetic parameters of reactions occurring during the process. Figures 2–5 are an illustration of DSC curves for non-catalytic and catalytic processes at different heating rates. As seen from pictures, strong evidence of the catalyst effect was found in both LTO and HTO regions, where peak temperatures shifted to lower values in the presence of Cu@Mn tallates at different heating rates and at different ratios. However, further data processing led to construction of Figure 6, which expresses differences between the peak temperatures (ΔT_p) of heavy oil

Table 1. Physical Properties of Ashalcha Heavy Oil at 20 °C

			elemental content (%)			SARA analysis (%)				
viscosity (mPa s)	density (g cm ⁻³)	API gravity (deg)	С	Н	Ν	S	saturate	aromatic	resin	asphaltene
11811	0.97	13.8	82.09	10.12	0.63	2.65	26.2 ± 0.5	44.1 ± 0.6	26.3 ± 0.5	4.5 ± 0.3



Figure 2. DSC curves for non-catalytic S(0) and catalytic S(1-5) oxidation of Ashalcha heavy oil at a 5 °C/min heating rate.



Figure 3. DSC curves for non-catalytic S(0) and catalytic S(1-5) oxidation of Ashalcha heavy oil at a 10 °C/min heating rate.



Figure 4. DSC curves for non-catalytic S(0) and catalytic S(1-5) oxidation of Ashalcha heavy oil at a 15 °C/min heating rate.

oxidation in the presence and absence of Cu@Mn tallates at different heating rates for LTO and HTO regions.

On the basis of the observation obtained from Figures 2-5 and Figure 6, we have chosen S(2) for further tests to show its efficiency on the stabilization of the combustion front during the oxidation process because it has shown relatively high shifting temperatures of peaks compared to other samples, excluding manganese tallates S(1) and copper tallates S(5), which have been studied previously.

3.2. Kinetic Study. The obtained kinetic parameters from Kissinger's plots of catalytic S(2) and non-catalytic S(0) oxidation of heavy oil (Figure 7) are grouped in Table 2. The interpretation of kinetic parameters, however, seems to be complicated because the catalyst affects them differently, where we observe a decrease in energy of activation during the catalytic process, which is a good indicator of the catalytic effect, whereas the frequency factor decreases as well and, hence, makes the estimation of the catalytic effect quite impossible based on the presented data because decreasing the



Figure 5. DSC curves for non-catalytic S(0) and catalytic S(1-5) oxidation of Ashalcha heavy oil at a 20 °C/min heating rate.



Figure 6. Differences between peak temperatures (ΔT_p) of non-catalytic S(0) and catalytic S(1–5) heavy oil oxidation in porous media for (top) LTO and (bottom) HTO at different heating rates.



Figure 7. Kissinger's plots for catalytic S(2) and non-catalytic S(0) oxidation of heavy oil (top is for LTO, and bottom is for HTO).

frequency factor is an indicator of the decreasing reaction rate. For this reason, we processed further to calculate reaction rate effective constants to shed light on how the catalyst affected the oxidation process. Figure 8 shows the reaction rate effective constants for LTO and HTO regions. It is clear that the reaction rate effective constant is higher in LTO, which may express a fast initiation of the combustion front. The same observation could be obtained in the HTO region, which is the region of combustion front propagation, where we can clearly see that the effective reaction rate constant is higher in the catalytic process compared to the non-catalytic process. This increasing rate constant witnesses the promotion of the combustion front in this region. Therefore, the use of this catalyst may play an important role in improving the process of *in situ* combustion.

The final step in our study was proposing an explanation for the catalytic effect obtained in the heavy oil oxidation process. Thus, we applied MALDI to determine the molecular weight of sulfur-containing compounds, especially asphaltene com-



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Figure 8. Variation of effective rate constants with the temperature for catalytic and non-catalytic oxidation (top is for LTO, and bottom is for HTO).

pounds. Figure 9 shows the MALDI spectrum of Ashalcha heavy oil in the absence of catalysts. It is clear that this oil contains a considerable amount of asphaltenes and resins, which are the main source of C–S and C–N bridges. As a result, the catalyst has a strong affinity to affect exactly these kinds of bridges (C–S and C–N) to lead to light-molecular-weight compounds³² and, therefore, to more fuel deposition, ending by promoting the combustion front during the process of *in situ* combustion.

4. CONCLUSION

In this paper, we have studied the effect of Cu@Mn tallates on stabilizing the combustion front during the process of *in situ*

	non-ca	atalytic	catalytic			
	LTO	НТО	LTO	НТО		
$E_{\rm a}$ (kJ/mol)	104.6 ± 1.8	145.8 ± 8.3	95.17 ± 2.4	120.6 ± 7.4		
$\log_{10} A^a$	9.8	11.9	8.7	8.5		

^{*a*}A in units of min⁻¹.



Figure 9. MALDI mass spectra of asphaltene compounds in Ashalcha heavy oil.

combustion. We applied DSC to highlight the kinetic parameters of the process. The obtained results showed that the combination of Mn tallates with Cu tallates results in enhancing the heavy oil oxidation process compared to the non-catalytic oxidation process. Moreover, the energy of activation decreases in the presence of a catalyst in the LTO region. In addition, it decreases in the HTO region, which leads to a high stabilization of the combustion front during HTO, where the effective reaction rate constant increased. In addition to this, we believe that Cu@Mn tallates highly affected the cracking of high-molecular-weight compounds, such as asphaltenes and resins, to lighter hydrocarbons and, therefore, upgrading oil in place, as was shown by MALDI, GC-MS, and SARA analysis. Moreover, the high melting point of tallate present as a ligand in the catalyst guarantees its high dispersion in the reaction medium, even at the HTO region, which is the main stage of combustion front propagation and stabilization. Further work will look into the investigation of tallate characteristics as stabilizers for transition metal oxide nanoparticles and their application in stabilizing the combustion front during in situ combustion.

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Notes

The authors declare no competing financial interest.

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